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Change of Plumb Line referred to the Axis of the Earth as found from the Results of the International Latitude Observations

(the second paper[1])

By **Eiiti Nisimura**

(Received July 30, 1937)

In continuation of the first study on the subject of this title by Prof. T. Shida and Prof. M. Matsuyama,[2] we analysed the data given in "Ergebnisse des Internationalen Breitendienstes von 1912.0 bis 1922.7 (von B. Wanach und H. Mahnkopf)." The Report contains the results of the six observing stations of north parallels ($\varphi = +39°8'$).

Mizusawa, Japan	$\lambda = -141° 8'$	period, 1912.0–1922.7
Tschardjui, Central Asia	− 63 35	1912.0–1919.4
Carloforte, Italy	− 8 19	1912.0–1922.7
Gaithersburg, East America	+ 77 12	1912.0–1915.0
Cincinnati, Middle America	+ 84 25	1912.0–1916.0
Ukiah, West America	+123 13	1912.0–1922.7

And the present study was made of the results of the three stations—Mizusawa, Carloforte, and Ukiah, because of their continuous observations during the whole period.

The daily corrections read from the most probable curve of latitude at each station given in the Report, were applied to each observed value of each star-pair to eliminate the proper variation of latitude. The residuals thus obtained for each star-pair were divided into six sets (each containing two groups of stars), and in each set were arranged according to the hour-angle of the true moon at the time of observation of each star-pair. The mean of these six means shows the correlation of the moon's hour-angle and the latitude. The number of star-pairs used and mean hourly values obtained for three stations are shown in Tables I, II, III and Figs. 1, 2, 3. Analysing harmonically, multiplying by the augmenting factor and reducing to the

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1. This paper was read at the Annual Meeting of the Physico-Mathematical Society of Japan, Osaka, 1935 April.

2. Mem. Coll. Sci. and Eng., Kyoto Imperial Univ., **4** (1912) 277–284.

mean inclination of the moon's orbit to the equator, the numerical values give the following expressions;

1912.0–1922.7

Mizusawa . . . . . $0.''0032 \cos(2t-260^\circ)\pm 0.''0014$
Carloforte . . . . . $0.''0118 \cos(2t-334^\circ)\pm 0.''0008$
Ukiah . . . . . $0.''0105 \cos(2t-11^\circ)\pm 0.''0013$

where t is the hour-angle of the true moon.

The slight difference between the present result and that formerly obtained in the first paper for Carloforte ($0.''00878 \cos(2t-356^\circ)$) is considered to be attributable partly to the point that in the present analysis the hour-angle of the true moon was used instead of the mean moon in the first study. The results obtained are certainly influenced by the secondary effect of the ocean tide, and for two stations—Carloforte and Ukiah—the roughly estimated values of these effects may account for the inconsistency of the results. For Mizusawa, the secondary effect alone can not serve as the quantitative interpretation of its peculiar result and the problem remains unexplained. We intend to obtain in the near future more accurate values by covering the longer period of observation with the same analysing method and eliminating the secondary effect of the ocean tide in more detailed points.

In conclusion the writer wishes to express his cordial appreciation to the late Prof. T. Shida, by whose kind suggestion and encouragement the present analysis was commenced and carried out. The writer's cordial thanks are also due to Messrs. K. Itô, T. Kawahara, and H. Hayasi for their kind help provided in the present computation.

Mizusawa

Table I.

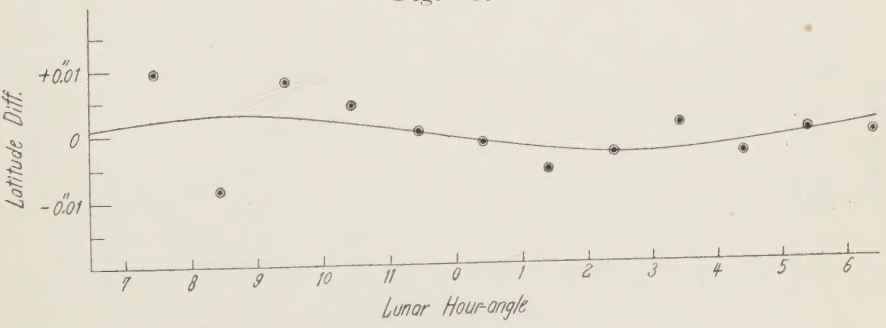
Number of Star-pairs

Hour-angle / Group	0^h	1	2	3	4	5	6	7	8	9	10	11
IV, V	204	228	251	242	247	239	241	259	293	290	286	273
VI, VII	264	263	299	323	315	298	286	243	236	239	283	270
VIII, IX	275	290	299	325	327	307	317	275	289	323	305	296
X, XI	310	316	308	280	306	299	318	290	326	349	337	308
XII, I	324	323	390	386	343	327	291	283	313	317	377	349
II, III	279	262	264	275	294	281	283	222	219	275	259	269
Sum	1656	1682	1811	1831	1832	1751	1736	1572	1676	1793	1847	1765

Mean Hourly Values

Hour-angle / Group	0^h	1	2	3	4	5	6	7	8	9	10	11
IV, V	″ 0.6823	6868	6905	6639	6741	6836	6675	7029	6271	6819	7002	6909
VI, VII	6564	6389	6445	6486	6529	6345	6339	6252	5969	6286	6264	6237
VIII, IX	5204	5320	5402	5765	5487	5659	5493	5434	5263	5393	5177	5150
X, XI	6008	6096	6169	6313	6161	6334	6454	6637	6739	6579	6332	6325
XII, I	6736	6517	6568	6617	6585	6566	6760	6663	6742	6905	6915	6884
II, III	6759	6648	6505	6424	6479	6448	6417	6761	6705	6687	6763	6712
Mean	″ 0.6349	6306	6332	6374	6330	6364	6356	6463	6281	6445	6409	6369
	−15	−58	−32	+10	−34	0	−8	+99	−83	+81	+45	+5

Fig. 1.



Carloforte

Table II.

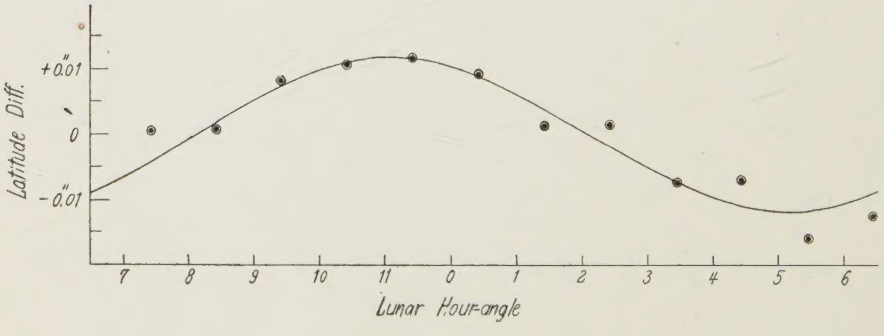
Number of Star-pairs

Hour-angle / Group	0^h	1	2	3	4	5	6	7	8	9	10	11
IV, V	227	203	215	208	226	262	305	294	239	226	238	225
VI, VII	277	294	288	292	307	287	285	257	257	250	259	239
VIII, IX	402	385	381	413	429	456	438	418	417	392	344	365
X, XI	621	586	593	601	656	719	720	756	757	745	704	659
XII, I	452	441	429	422	433	416	429	433	438	460	484	484
II, III	232	222	197	202	211	235	245	208	212	206	199	222
Sum	2211	2131	2103	2138	2262	2375	2422	2366	2320	2279	2228	2194

Mean Hourly Values

Hour-angle / Group	0^h	1	2	3	4	5	6	7	8	9	10	11
	″											
IV, V	1.0436	1.0059	1.0191	1.0060	.9918	.9737	.9798	.9789	.9825	1.0219	1.0227	1.0356
VI, VII	.9850	.9856	.9899	.9828	.9833	.9804	.9595	.9582	.9664	.9611	.9615	.9690
VIII, IX	.8791	.8746	.8782	.8852	.9042	.8920	.8941	.9010	.8834	.8774	.8684	.8761
X, XI	.9708	.9780	.9581	.9607	.9683	.9714	.9791	.9951	.9962	.9991	.9952	.9761
XII, I	1.0174	1.0064	1.0014	.9927	.9867	.9845	.9966	1.0149	1.0256	1.0243	1.0328	1.0358
II, III	1.0145	1.0121	1.0175	.9819	.9794	.9573	.9734	1.0094	1.0068	1.0221	1.0380	1.0312
	″											
Mean	0.9851	9771	9774	9682	9689	9599	9637	9762	9768	9843	9864	9873
	+92	+12	+15	−77	−70	−160	−122	+3	+9	+84	+105	+114

Fig. 2



Ukiah

Table III.

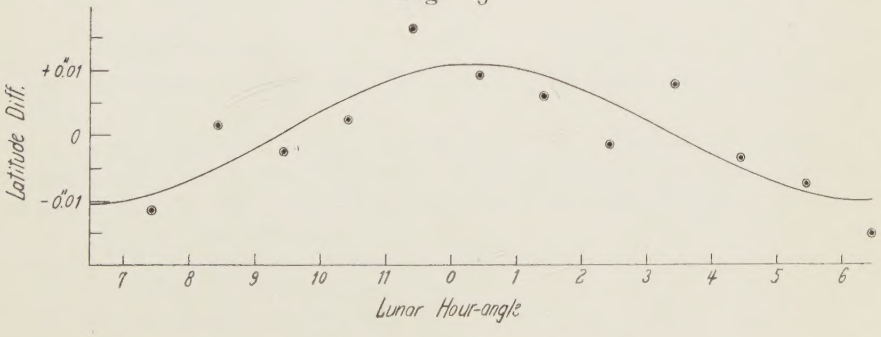
Number of Star-pairs

Group \ Hour-angle	0h	1	2	3	4	5	6	7	8	9	10	11
IV, V	166	176	171	183	193	167	173	190	189	181	154	144
VI, VII	167	158	159	187	209	230	208	188	193	204	234	200
VIII, IX	223	201	234	251	277	259	254	244	269	270	235	235
X, XI	357	342	376	383	366	390	426	458	413	405	389	375
XII, I	339	352	366	370	376	369	348	361	348	336	345	363
II, III	170	164	190	206	224	221	211	205	206	190	191	186
Sum	1422	1393	1496	1580	1645	1636	1620	1646	1618	1586	1548	1503

Mean Hourly Values

Group \ Hour-angle	0h	1	2	3	4	5	6	7	8	9	10	11
	″											
IV, V	0.2648	2397	2022	2338	1955	2057	1602	1797	1811	2085	1926	2649
VI, VII	1519	1589	1718	1561	1515	1532	1375	1209	1456	1425	1191	1733
VIII, IX	449	482	507	351	464	460	465	523	645	443	748	337
X, XI	1088	1061	1044	1202	1276	1153	1234	1196	1452	1252	1451	1128
XII, I	1825	1870	1589	1615	1588	1526	1706	1764	1695	1852	1879	2275
II, III	2062	1998	2051	2444	2014	1838	1719	1857	2089	1830	1994	1920
	″											
Mean	0.1598	1566	1489	1585	1469	1428	1350	1391	1525	1481	1531	1674
	+91	+59	−18	+78	−38	−78	−157	−116	+18	−26	+24	+167

Fig. 3



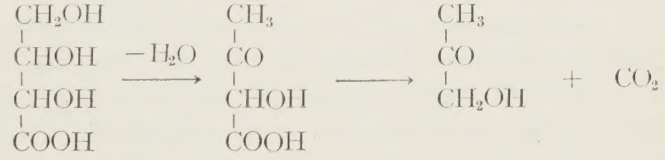
On the Action of Phosphate upon Hexoses III

Simultaneous Formation of Acetol and Pyruvic Acid from Glucose

By Ryuzaburo Nodzu, Kiyotada Matsui, Ryozo Goto and Sango Kunichika

(Received Oct. 4, 1937)

Formation of acetol from glucose by the influence of some alkaline reagents has often been reported by several investigators[1]. It seems, however, still quite obscure how the acetol is formed. Nef[2] postulated the acetol to be a reduction product of methylglyoxal which splits primarily from the sugar. As it is well recognized that glucose splits into two molecules of methylglyoxal by the action of alkalis, it seems quite possible the latter may in turn undergo dismutation, giving acetol and pyruvic acid[3]. On the other hand, Baudisch and Deuel[4] argued acetol to be a primary fission product of the sugar, since in contrast to glucose, methylglyoxal gave on distillation with sodium hydrogen carbonate only a very small quantity of acetol. But they said nothing about the product which should be formed from a glucose molecule simultaneously with acetol. Löb[5] assumed as an intermediate of acetol erythronic acid which may be formed from glucose and decomposed to acetol according to the following scheme:



Erythronic acid Acetol

This assumption implies that the acetol is formed by successive cleav-

1. A. Emmerling and G. Loges, Ber., **16** (1883), 837; G. Pinkus, Ber., **31** (1898), 31; O. Baudisch, Biochem. Z., **89** (1918), 279; O. Baudisch and H. J. Deuel, J. Am. Chem. Soc., **44** (1922), 1585; R. Nodzu and R. Goto, Bull. Chem. Soc. Japan, **11** (1936), 381.
2. J. U. Nef, Ann., **335** (1904), 255.
3. C. Neuberg, Biochem. Z., **49** (1913), 502.
4. O. Baudisch and H. J. Deuel, Loc. cit.
5. W. Löb, Biochem. Z., **12** (1908), 78.

ages of C_1 or C_2- (but no C_3-) fragment, from a molecule of glucose or rather of its intramolecular transformation product.

In our previous work[1], it was observed that even when glucose is distilled with an acid (pH, 4–7) concentrated (about 40%) solution of potassium phosphate, acetol is found (in a yield about 5% of the sugar) in the distillate. Now, in the distillation residue, we were able to identify pyruvic acid as its 2 : 4-dinitrophenylhydrazone. But the amount of the acid was not large, i. e., at the largest 0.5% on the basis of glucose used. It should not obviously be hastily concluded that the pyruvic acid is a primary fission product of glucose, since such a small amount of the acid might be formed in the course of the distillation by autoxidation of some other primary C_3 fission products. Actually acetol and methylglyoxal were converted to the acid to a small extent under experimental conditions, but no lactic acid.

When, however, glucose was digested at 105–110°[2] with the phosphate solution under painfully air-free conditions—a vacuum higher than the order of 10^{-5}mm.—pyruvic acid was again found in the digestion product, though its yield was somewhat inferior to that in the distillation experiment. From the same reaction product, only traces of acetol could be obtained as its 2 : 4-dinitrophenylosazone. The yields of acetol and pyruvic acid do not necessarily imply that both were formed only in such scanty amounts. Acetol is well known to be an unstable substance. Pyruvic acid was only recoverable some to 50% after being subjected with the phosphate solution to the same distillation process as in the case of glucose, and to our interest, almost entirely disappeared when similarly treated in the presence of glucose. Moreover, methylsuccinic acid[3]—a condensation product of pyruvic acid—was found along with pyruvic acid in the distillation residue of glucose. Thus both acetol and pyruvic acid seem quite unstable and may suffer various transformations under experimental conditions. In view of the preceding results, there seems to be no doubt that by the action of the phosphate solution, glucose gives pyruvic acid simultaneously with acetol without any intervention of autoxidation.

On the other hand, methylglyoxal or d,l-glyceric aldehyde—a supposed precursor of the former—afforded on distillation with the

1. R. Nodzu and K. Matsui, Bull. Chem. Soc. Japan, **10** (1935), 122, 467.
2. The figures correspond approximately to the boiling temperature of the concentrated potassium phosphate solution.
3. L. Wolff, Ann., **317** (1901), 1.

phosphate solution mainly methylglyoxal and only a small quantity of acetol. This result is quite inconsistent with that from glucose, and indicates clearly that the simultaneous formation of acetol and pyruvic acid may not occur by a predictable route: glucose → 2 glyceric aldehyde → 2 methylglyoxal → acetol + pyruvic acid. Admitted, however, that under certain conditions a molecule of glucose decomposes into two molecules of methylglyoxal:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{-2H_2O} \underset{\text{Methylglyoxal}}{2\,CH_3COCHO},$$

it is quite possible that under other conditions it may split disproportionally without intervention of methylglyoxal or glyceric aldehyde into one molecule each of acetol and pyruvic acid:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{-H_2O} \underset{\text{Acetol}}{CH_3COCH_2OH} + \underset{\text{Pyruvic acid}}{CH_3COCOOH}$$

And it seems very probable that the simultaneous formation of acetol and pyruvic acid may be ascribed rather to this process.

In the distillation experiment on glucose with the acid phosphate solution, the production of methylglyoxal was very small as already shown in the previous paper and that of lactic acid also far inferior to that by the action of some alkaline reagents on glucose. Since under the experimental conditions lactic acid was quite stable and methylglyoxal also tolerably stable—perhaps it transforms partly into the acid—, the decomposition of glucose favorable in alkaline media: Glucose → 2 methylglyoxal → 2 lactic acid, seems markedly depressed here in an acid medium.

As to whether the mechanism described above is also applicable to the formation of acetol from glucose by the influence of alkalis, further study is in progress.

Experimental Part.

Formation of Pyruvic Acid. In the same way as described in the previous paper, glucose in a certain volume of about 40% solution of potassium phosphate (pH, 4.5 or 6.3) was distilled, keeping the volume constant by adding fresh water in small portions, and the distillate was analysed for acetol, diacetyl and methylglyoxal as their semicarbazones. The distillation residue was made up to one and a half in volume by addition of six-normal hydrochloric acid and a

precipitate soon formed was filtered off. To the filtrate was added an adequate volume of 2 : 4-dinitrophenylhydrazine reagent (1% in 2N-hydrochloric acid) and the mixture was kept over night at room temperature. A reddish-brown precipitate thus formed, was a quite complex mixture. From this, pyruvic acid-2 : 4-dinitrophenylhydrazone was isolated by exploiting the description of Case[1]. The precipitate was dissolved in a mixture of ethylacetate and toluene, and the solution was extracted by 25% sodium carbonate solution. The extract was then acidified with concentrated hydrochloric acid so as to precipitate the hydrazone. Since the precipitate of hydrazone was still contaminated with other compounds, it was again treated in the same way. Then it was recrystallized from alcohol. The melting points of the samples prepared in this way lay between 209° and 212°. After another recrystallization from alcohol, it melted at 215° and showed no depression in the mixed melting point (Found : N, 20.6. Calc. for $C_9H_3O_6N_4$: N, 20.9%).

The processes of isolation and purification of the hydrazone are tedious and wasteful, obviously not quantitative. Since, however, the crude hydrazone is always contaminated with some substances which give by alkali a coloration similar to that of the hydrazone, the colorimetry of Case can not be used here.

Amounts of the hydrazone actually isolated were always very meagre and two results from our experimental protocols are quoted in Table I.

Table I.

Glucose 20 g., 40% Solution of K-phosphate 200 c.c.

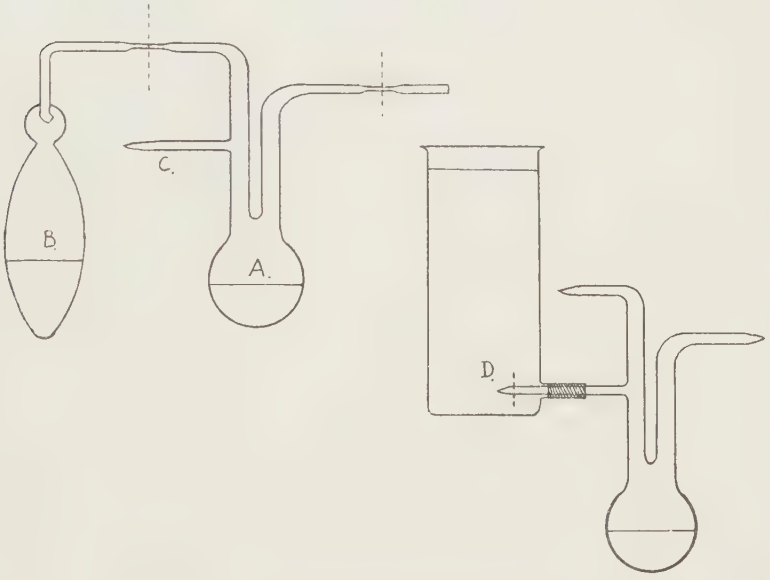
pH	4.5	6.4
Distill. duration (hour)	15	4.5
Distillate (c.c.)	2.340	820
Diacetyl-bis-semicarbazone (g.)	<0.01	—
Methylglyoxal-bis-semicarbazone (g.)	<0.01	—
Acetol-semicarbazone (g.)	0.32	0.17
Pyruvic acid-2 : 4-dinitrophenylhydrazone (m. p. 209–212°) (g.)	0.31	0.24

Formation of Pyruvic Acid under air-free conditions. 100 c.c. of the potassium phosphate solution of a certain pH, were evaporated

1. E. M. Case, Biochem. J., **26** (1932), 753.

to dryness. It was then powdered and mixed with 10 g. of glucose. This mixture was put in a glass flask A (Fig. 1.) of about 250 c.c. capacity. A glass bottle B (300 c.c.) contained about 150 c.c. of a mixture of stannous chloride and sodium hydroxide and water (0.5 :

Fig. 1



0.1 : 100). Cooling bottle B with liquid oxygen and warming flask A up to 80°, the whole system was highly evacuated up to a pressure of 10^{-6}mm. order.

Now the cooling and the warming devices were taken away, and anew flask A was cooled with liquid oxygen and bottle B was warmed very gradually up to the temperature of the human body. When the volume of water condensed in flask A reached 100 c.c., the flask was sealed in a blow-pipe at the two points marked with the dotted lines in the figure.

After digesting the flask content at 105–110° for a certain interval, it was brought to room temperature and scratched with a file near the end of side tube C. Side tube C was then connected with a thick rubber tubing to another side tube of a container D (about 500 c.c.) which held a sufficient quantity of the 2 : 4-dinitrophenylhydrazine reagent freed from air by boiling and cooling under a nitrogen current. Now side tube C was broken at the scratch by a pinch to let the hydrazine reagent spout into flask A. The precipitate thus

formed was analysed for pyruvic acid hydrazone as usual. In each experiment with the phosphate solution of pH, 6.4 (digestion interval 12 hours) and 4.5 (digestion interval 24 hours), about 0.01 g. of the hydrazone (m. p. 210–212°) was obtained. In these experiments, only traces of acetol osazone were obtained in an impure state (m. p. 290°–). This fact may be due partly to the difficulty of its separation from other products and partly to the disappearance of acetol once formed which might occur under the experimental conditions.

Formation of Lactic Acid. A mixture of 10 g. glucose and 100 c.c. of the phosphate solution of a certain pH was distilled as usual. When the distillate amounted to 2000 c.c. (distillation duration about 20 hours), lactic acid was isolated from the distillation residue as its zinc salt following Evans' description[1] and identified by Deniges' reaction. Also the same residue as above was quantitatively analysed for the acid by means of Tanaka and Endo's method[2]. Three experimental results with the phosphate solutions of different pH values are brought together in Table II.

Table II.

Glucose 10 g., 40% Solution of K-phosphate 100 c.c.

pH	4.5	6.4	8.4*
Zn-lactate	?	+	++
Lactic acid (g.)	0.06	0.10	0.56

*Na_2HPO_4 was used.

Formation of Methylsuccinic Acid. According to Wolff[3], pyruvic acid transforms spontaneously or especially by the influence of mineral acid, to methylsuccinic acid by way of α-ketovalerolactonecarboxylic acid. This transformation is to be expected under experimental conditions.

A distillation residue (distillation duration about 20 hours) from a mixture of 30 g. glucose and 300 c.c. of the potassium phosphate solution (pH 6.4) was neutralized with caustic potash and evaporated to syrup. After treatment with ether, the syrup was made strongly acidic by sulphuric acid, and then shaken with ether several times so as to extract acidic substances. The extract from which ether had been driven, was kept for about ten days in a desiccator over sulphuric

1. W. L. Evans and coworkers, J. Am. Chem. Soc., **48** (1926), 2665.
2. S. Tanaka and M. Endo, Biochem. Z., **210** (1929), 120.
3. L. Wolff, loc. cit.

acid. Some colourless fine crystals appeared in a viscous mass from which they were with difficulty separated by means of a porous plate. After a recrystallization from a mixture of ether and petroleum benzene, they weighed only 0.006 g. and melted at 109–110°, and showed no lowering of the melting point on admixing with an authentic specimen of methylsuccinic acid (Found : C, 45.4 ; H, 6.4. Calc. for $C_5H_8O_4$: C, 45.5 ; H, 6.1%) which was prepared from pyruvic acid according to Wolff.

α-Ketovalerolactonecarboxylic acid was in vain attempted to be identified as its phenylhydrazone in an identical distillation residue.

Instability of Pyruvic Acid. In the following experiments, a freshly distilled pyruvic acid (b. p. 48–50°/8 mm.) was used.

A solution of 0.105 g. of pyruvic acid (1 mol) in 50 c.c. of water was made about two-normal in regard to hydrochloric acid by addition of six-normal hydrochloric acid and mixed with 36 c.c. (1.5 mols) of the 2 : 4-dinitrophenylhydrazine reagent and left to stand at room temperature for completion of the precipitation. The precipitate of pyruvic acid-2 : 4-dinitrophenylhydrazone was filtered (filtrate A) and dried. It amounted to 0.301 g., corresponding to 94.2%[1] of pyruvic acid used and it melted at 215°. This sample was dissolved in 6 c.c. of a concentrated solution (about 25%) of sodium carbonate and the solution was filtered, and then the hydrazone was reprecipitated by addition of concentrated hydrochloric acid to the filtrate. It weighed 0.2964 g. which corresponds to 92.7% of the original pyruvic acid. In order to see if any material of the hydrazone remained in the filtrate A, Case's procedure was adopted. The filtrate was extracted with ethylacetate. After the ethylacetate liquor evaporated to a small volume, it was mixed with tenfold its volume of toluene and the mixture was filtered. The filtrate was well shaken with a few c.c. of the concentrated soda solution. However on acidifying the soda solution with hydrochloric acid none of the hydrazone was precipitated.

From a mixture of 0.25 g. of pyruvic acid and 50 c.c. of the concentrated phosphate solution (pH, 6.4), by the same procedure as above, was obtained 0.715 g. of the hydrazone (m. p. 214°, 94.0%) which decreased interestingly to 0.604 g. (m. p. 215°, 79.2%) after a purification by the soda treatment. However, after the same mixture

1. The datum differs noticeably from that of Simon and Neuberg, who recovered the acid up to 99% in a like experiment. (Biochem. Z., **232** (1931), 479.) The discrepancy might be due to a difference in purity of the materials.

of pyruvic acid and the phosphate solution was subjected to distillation for about 10 hours (distillate 1,000 c.c.), from the distillation residue was obtained 0.37 g. of the crude hydrazone (m. p. 210°–, 50%) which on further analysis resolved into 0.1 g. of the pure hydrazone (m. p. 215°), and some other acidic and neutral substances. It was not possible to identify pyruvic acid in the distillate.

The presence of glucose in the mixture of pyruvic acid and the phosphate solution made isolation of the hydrazone difficult—it was necessary to follow Case's process—and seemed to accelarate transformation of the acid. After it had stood at room temperature for an hour, a mixture of 3 g. of glucose and 0.02 g. of pyruvic acid and 30 c.c. of the phosphate solution (pH, 5.4) was analysed by Case's method for the acid, and 0.043 g. of the hydrazone (m. p. 214°, 72%) was obtained. When however, samples of the same mixture were distilled for an hour (distillate 55 c.c.) and for 16 hours (distillate 750 c.c.), 0.027 g. (m. p. 214°, 45%) and less than 0.001 g. (m. p. 190°–) of the hydrazone was isolated from the respective distillation residues.

Distillation of Glyceric Aldehyde and Methylglyoxal. d, l-Glyceric aldehyde was prepared by way of acrolein acetal from glycerine, following the description of Witzemann[1], and melted at 128°. Methylglyoxal* (b. p. 39–41°/15 mm.) was obtained by oxidation of acetone by means of selenium dioxide[2].

Each 2 g. of these two materials were respectively distilled with 50 c.c. of the phosphate solution of different pH values. The distillates and the distillation residues were analysed, and the results are summarized in Tables III and IV.

Table III.

Glyceric aldehyde 2 g. in 200 c.c. H_2O, 40% Solution of K-phosphate.

pH	4.5	6.3	9.3
Distillation duration (hour)†	22	7	7
Distillate (c.c.)	1,700	500	500
Diacetyl-bis-semicarbazone (g.)	0	0.01	0.01
Methylglyoxal-bis-semicarbazone (g.)	0.86	0.04	0
Acetol-semicarbazone (g.)	0	0.02	0.14
Pyruvic acid-2 : 4-dinitrophenylhydrazone (m. p. 210–212°) (g.)	0.07	0.02	0

1. E. I. Witzemann, J. Am. Chem. Soc. **36** (1914), 1908.
2. H. L. Riley, J. F. Morley and N. A. C. Friend, J. Chem. Soc., (1932), 1875.

* It was always contaminated with traces of pyruvic acid.

Table IV.

Methylglyoxal 2 g. in 200 c.c. H_2O, 40% Solution of K-phosphate.

pH	4.6	6.3	9.3
Distillation duration (hour)†	8	8	8
Distillate (c.c.)	600	650	620
Diacetyl-bis-semicarbazone (g.)	0	<0.01	0.02
Methylglyoxal-bis-semicarbazone (g.)	2.2	0.4	0
Acetol-semicarbazone (g.)	0	trace	0.02
Pyruvic acid-2 : 4-dinitrophenylhydrazone (m. p. 209—211°) (g.)	0.02	0.01	0

† The distillation was continued until no more iodoform reaction was observed in the distillate.

The actual formation of pyruvic acid in these two series of experiments led us to conclude that methylglyoxal suffers autoxydation. The acetol formed (especially in the alkaline region) might rather be a secondary product from some C_6-compound produced by condensation of glyceric aldehyde or methylglyoxal.

It is also worth noticing that methylglyoxal does not distill over from the alkaline solution.

Distillation of Acetol. Acetol (b. p. 53–54°/18 mm.) was prepared from monobromoacetone by the method of Levene and Walti[1] uncontaminated with pyruvic acid.

The distillation of 1 g. of acetol (in 500c.c. H_2O) with 50 c.c. of the phosphate solution (pH 6.4) was continued for 7.5 hours and 778 c.c. of the distillate were obtained. On analysis the distillate gave 1.20 g. of acetol-semicarbazone (0.68 g. as acetol), traces of methylglyoxal-bis-semicarbazone, and the distillation residue afforded 0.03 g. of pyruvic acid 2 : 4-dinitrophenylhydrazone (m. p. 214°).

This showed that acetol is also susceptible to autoxydation.

Distillation of Lactic Acid. 0.8 g. of lactide (m. p. 122°) was refluxed for 3 hours with 150 c.c. of N/10 soda solution. The product was neutralized by hydrochloric acid and made up to 500 c.c. by addition of water. Adding lactic acid solution thus prepared in small portions, 50 c.c. of the phosphate solution (pH 4.5, 50 c.c.) was distilled. The distillate gave no iodoform reaction. After continuing the distillation for 14 hours (distillate 1000 c.c.), an appreciable quantity of lactic acid in the form of zinc salt and a trace of a 2 : 4-dinitrophenylhydrazone (m. p. 204–208°) were obtained from the distillation residue. With

1 "Org. Syntheses." Vol. X. p. 1. (1930).

the phosphate solution of pH 9.3 the experimental results were quite alike.

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